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Ab Initio Calculations of Vibrational Frequencies in a Glassy State of Selenium

(Pengiraan *Ab Initio* bagi Frekuensi Getaran pada Selenium Berkeadaan Kaca)

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ABSTRACT

We used the density functional theory to calculate the vibrational frequencies of clusters of atoms. We obtained the bond distances and angles for which the energy of the Schrödinger equation is minimum. We found the bond distance between two Se atoms to be 232.1 pm when double zeta wave function was used. The frequency of oscillations was calculated to be 325.3 cm^{-1} but the intensity was zero because Se_2 molecules were present in a very small number. When polarised double zeta wave function (DZP) was used, the bond length of Se_2 was found to be 223.1 pm and the frequency is 367.4 cm^{-1} . Similarly for other clusters of selenium, we calculated the frequencies and compared with the experimental data. The experimental Raman spectra give 250 cm^{-1} for a selenium glass. By comparing the experimental frequencies with those calculated we found that linear Se_3 was present in the glass. This indicates the possibility of linear growth in the glass.

Keywords: Density functional theory; glass; raman spectra; selenium; vibrational frequencies

ABSTRAK

Kami menggunakan teori fungsi ketumpatan untuk membuat pengiraan bagi frekuensi getaran bagi kelompok atom. Apabila tenaga persamaan Schrödinger diminimumkan, kami dapat mengukur panjang ikatan dan sudut bagi atom-atom. Panjang ikatan bagi dua atom Se adalah 232.1 pm dengan menggunakan fungsi ikatan zeta berganda. Frekuensinya adalah 325.3 cm^{-1} tetapi keamatannya adalah sifar disebabkan kehadiran sangat sedikit molekul Se_2 . Apabila fungsi gelombang zeta berganda berketub digunakan, panjang ikatan adalah 223.1 pm dan frekuensinya adalah 367.4 cm^{-1} . Sama juga bagi kelompok selenium yang lain, kami mendapatkan frekuensi gelombang untuk dibandingkan dengan data eksperimen. Data eksperimen bagi spektrum Raman menunjukkan nilai 250 cm^{-1} bagi kaca selenium. Perbandingan dengan data eksperimen menunjukkan Se_3 linear wujud dalam kaca. Ini menunjukkan kemungkinan pertumbuhan secara linear dalam kaca.

Kata kunci: Frekuensi getaran; kaca; spektrum Raman; selenium; teori fungsi ketumpatan

INTRODUCTION

The study of strength of glasses is important for the understanding of its elastic properties. Some glasses exhibit the phenomenon of self-organization (Phillips 1981). In some glasses, there are soft phonons (Thorpe 1983), the frequencies of which go to zero. In Raman spectroscopy, the frequency of the soft phonon becomes so small that it merges with the Rayleigh line. The experimental measurements of the Raman spectra have been carried out by Boolchand (Boolchand 2001; Wang et al. 2001). In recent years, we have calculated the vibrational frequencies from the first principles (Devi et al. 2005; Kassim et al. 2007). In GeSi, the calculated values (Devi et al. 2005) of the vibrational frequencies are in good agreement with those found experimentally from the Raman spectra. In the case of GePS glass (Kassim et al. 2007) the values are close to the experimental values obtained from the Raman spectra. We have therefore made an effort to determine the vibrational frequencies in selenium metal. We studied

many different models by using the density-functional theory and calculated the vibrational frequencies in each case. The smallest molecule Se_2 was not formed at all and there are a minimum number of atoms before which the system can stabilise.

In this paper, we report our calculation of vibrational frequencies of clusters of Se atoms. The density functional theory with local density approximation (LDA) was used to solve the Schrödinger equation. The Se clusters were optimized to the minimum energy before we get the vibrational frequencies. We calculated the vibrational frequencies by using the Amsterdam density functional (ADF) program with double zeta wave functions using the Intel Core 2 Duo computer.

In our calculation, we found that Se_3 is the smallest cluster for which the stability was obtained and the vibrational frequencies were calculated. The calculation was performed by having double zeta wave functions with and without polarisation. Many different clusters

have been studied. The molecules, Se_2 , Se_3 , Se_3 -linear, Se_3 -ring, Se_4 -linear, Se_4 -pyramidal, Se_4 -square, Se_5 -linear, Se_5 -pyramidal and Se_5 -ring, have been optimised and their bond lengths were obtained for the minimum energy. The vibrational frequencies have been calculated in each case. The calculated frequencies are compared with those found in the experimentally measured Raman spectra of Se glass. This comparison showed that Se_3 was present in the glass and Se_2 was not stable as evidence from its zero intensity.

CALCULATED FREQUENCIES

The density functional theory was used to make a model of several atoms. The energy of the Schrödinger equation was minimised to obtain the bond lengths and angles in the cluster models. The vibrational frequencies were obtained for the optimised clusters. We make several clusters with a variety of wave functions. The double zeta wave functions were used with and without the polarisation. Some of our clusters are described below.

Se_2 -linear cluster. The Se_2 molecule was considered and optimised for the minimum energy. The optimised bond length was found to be 232.1 pm. In this case, the intensity of the vibrational spectrum is almost zero, indicating that the number of molecules formed was very small. The vibrational frequency was found to be 325.3 cm^{-1} but zero intensity shows that it is unlikely to be observed. The double zeta wave function (DZ) is then replaced by the polarised wave function. The double zeta wave function with polarization (DZP) changed the bond distance to 223.1 pm and the vibrational frequency to 367.4 cm^{-1} but the intensity continued to be negligibly small. The intensity of vibrations of the A_1 mode of NH_3 in the DZP becomes very small such as 0.7 km/mole in local density approximation (LDA) compared with 57.8 km/mole for the doubly degenerate mode as discussed by Fan and Zeigler (1995). The intensity of the linear diatomic Se_2 molecule

found by us is indeed zero so that we can assume that these molecules do not exist, except in the negligibly small quantity. This raises an interesting question, namely what is vibrating in the pure selenium glass?

Se_3 -linear. The DZ wave function gave the bond length 248.6 pm and the vibrational frequencies of 247.2 cm^{-1} for the optimised linear arrangement of three atoms with strong intensity of ~ 35.7 km/mole. The DZP for this system gave 238.3 pm for the bond length, 260.1 cm^{-1} for the frequency and 68.6 km/mole for the intensity.

Se_3 -ring. The three atoms of Se were arranged in a triangular form. The DZ wave function gave 253.8 pm as the bond distance with degenerate two values of the vibrational frequency of 217.2 cm^{-1} each. The DZP wave function for this triangular molecule gave 241.3 pm for the bond distance and 248.38 cm^{-1} for the vibrational frequency with intensity 0.0639 km/mole. A strong vibrational spectrum was obtained as shown in Figure 1.

Se_4 -linear. The DZ wave function for four atoms of Se in a linear configuration gave the bond length of 233.1 pm and a vibrational frequency of 313.5 cm^{-1} with strong intensity of 33.0 km/mole, while the DZP wave function gave the bond length of 233.0 pm with frequency 313.79 cm^{-1} .

Se_4 -pyramidal. The three atoms sit on a triangle and the fourth atom on the top position so that a pyramidal molecule is formed. The DZ wave function gave 287.4 pm for the bond length and three values of the vibrational frequency of 1183.7 cm^{-1} . The DZP gave 271.3 pm for the bond length and 50.9 cm^{-1} for the frequency. Therefore, the effect of polarisation in this model was very strong.

Se_4 -square. The set of 4 atoms on the corners of a square when optimised for the minimum energy using the density-functional theory with DZ wave function gave 257.3 pm for the bond length and 229.07 cm^{-1} for a doubly degenerate vibration. When DZP was used the optimised bond length became 254.0 pm and the frequency got shifted to 261.7 cm^{-1} with intensity 1.13 km/mole.

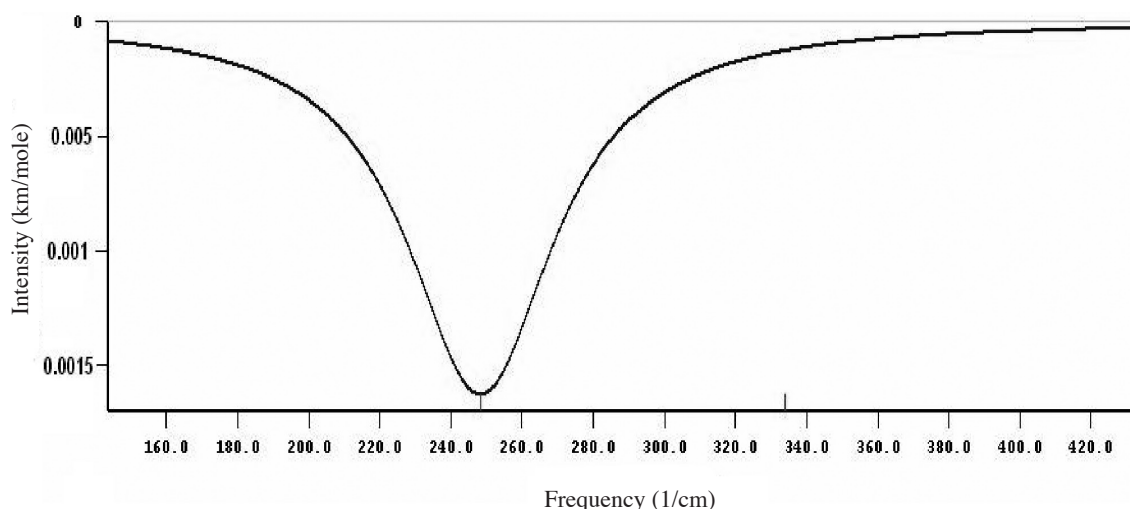


FIGURE 1. The vibrational spectrum of Se_3 ring calculated from first principles

Se₅-linear. Five atoms of Se arranged linearly give 258.1 pm for the bond length and weak vibrations, with DZ wave function, at 31.7 cm⁻¹ (two values of intensity 0.089 km/mole each) and 147.9 cm⁻¹ (two values of intensity 0.039 km/mole each). There was another vibration at 225.7 cm⁻¹ (intensity 24.3 km/mole) and strong vibration at 256.8 cm⁻¹ (intensity 97.4 km/mole). Considering the intensities, the strong vibration is located at 256.8 cm⁻¹. The DZP wave function gave 229.5 pm for the bond length and weak oscillations at 39.69 cm⁻¹ (two values 0.0008 km/mole each), 194.8 cm⁻¹ (intensity 19.38 km/mole) and strong vibration at 303.4 cm⁻¹ (intensity 25.4 km/mole).

Se₅-pyramidal. There were 4 atoms in the base and one on top. The DZ wave functions give 274.0 pm for the bond length and 113.7 cm⁻¹ (intensity 16.3 km/mole), with strong oscillation at 242.09 cm⁻¹ (intensity 0.418 km/mole). The polarised wave function DZP gave 274.0 pm for the bond length and 131.37 cm⁻¹ (0.003 km/mole) for a weak vibration and 235.0 cm⁻¹ (12.06 km/mole) for a doubly degenerate strong vibration.

Se₅-ring. The ring model with five atoms by using DZ wave function gives 252.1 pm for the bond length and the ring frequency was 232.4 cm⁻¹ (2.7 km/mole). The polarised wave function gave the bond length of 241.4 pm and the ring frequency of 259.8 cm⁻¹ (1.01 km/mole).

RAMAN SPECTRA

The most detailed experimental studies of the Raman spectra in glasses have been performed by Boolchand (2001). The spectra of Ge_xSe_{1-x} with varying concentration lead to the discovery of rigidity transition. We have also computed the Ge–Se bond and its vibrational frequencies (Jemali et al. 2008). During this study it was clear that Se–Se bond was not well understood. According to the experimental study, Se–Se stretching mode of Se_n–chain (chain mode) occurs at about 250 cm⁻¹. Our calculations showed that this experimental value occurred in Se₃ with Se₃-linear oscillating at 247.2 cm⁻¹ while Se₃-ring oscillates at 248.3 cm⁻¹. This calculation showed that Se₂ were not formed due to the metallic character of the glass.

CONCLUSION

We have performed the ab initio calculations using density functional theory with local density approximation for vibrational frequencies in several different models of selenium. From these calculations we find that Se₃ molecules were formed in the Se glass. The calculated values were close to those measured in Se glass.

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